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# EVALUATION OF DIONEX
# ANION MICROMEMBRANE SUPPRESSOR
# IN
# THE ION CHROMATOGRAPHY LABORATORY
# WATER QUALITY SECTION

Grace Denny
Bernie Wright
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Ontario Ministry of the Environment
Laboratory Services Branch

December, 1992

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## Introduction

Ion Chromatography (IC), coupled with conductivity detector is a powerful analytical technique for the separation and detection of ions(1,2). Since the introduction of IC in the Water Quality Section (WQS) in 1977(3), three types of suppressors have been used. They are column suppressor, fibre suppressor and micromembrane suppressor.

In terms of historical development of the suppressor devices(1), sulfonated polyethylene surgical tubing, the earlier form of fibre suppressor, had been used to study the possibility of dialysis concentration of magnesium from seawater. In 1971 Small(1) attempted the first anion separation by suppressed IC using a membrane suppressor. However the membranes were brittle and would burst under mild excess pressure. Furthermore, column suppressors proved to be more robust and were so easily prepared that the membrane approach was abandoned in the early, rapid development of suppressed IC. Dionex began marketing the complete ion chromatographic system, including the column suppressor, in 1975. The suppressor consists of a column packed with a high capacity ion exchange resin (Figure 1). For the sodium bicarbonate and carbonate eluent used in the IC Lab, its purpose is to remove the sodium ions and to replace them with hydrogen ions. This "stripper" column has helped to popularize the IC analytical technique for ions with varying degrees of conductance. However it is not without problems. Some of the drawbacks are:

1. The suppressor column inevitably contains void volume which causes random flow path. This produces undesirable band spreading. The separated bands become slightly merged and the end result is loss in peak resolution.

2. As the column suppressor ages, the amount of active exchange sites decreases. The negative water dip drifts and may eventually interfere with the peak measurement of fluoride and chloride.

3. The column suppressor's ability to exchange the undesirable eluent ions is limited and it needs replacement or regeneration when its capacity is exhausted. Replacement is never considered to be cost effective and therefore the suppressor is invariably regenerated. To accomplish this, the ion chromatographic system has to be shut down, the suppressor column regenerated with acid, flushed with water and equilibrated before the background conductance drops to an acceptable low and steady level.

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*We thank M. Rawlings for bringing reference paper number 6 to our attention and for his review of this report.*

4. In the suppressor column used for the separation of anions, if the analyte ion forms a weak acid such as acetic acid in the suppressor, it will be slightly retained by the suppressor (Donnan effect). The degree of retention depends on the equilibrium between the anion and its acid. As the hydronium ions are depleted from the suppressor column, the anion form of the analyte is favoured and its retention time decreases. This results in peak drift of the analyte anion.

To alleviate the above problems, Dionex brought out the fibre suppressor in 1983. This device is based on a different ion exchange mechanism, in which the sodium ions migrate through a semi-permeable tubing from the eluent side to the regenerant side in exchange for the hydrogen ions (Figure 2A). The tubing is wrapped around a spindle and its entire length is enclosed in a shell with openings at both ends for regenerant flow. The construction of the unit was modified by Wright(4) because of frequent baseline drift. The modified fibre (Figure 2B) is constructed of two concentric pieces of tubing. The inner tube where the eluent flows is made of sulfonated polyethylene and packed with polymer beads of polystyrene divinyl benzene. The beads fill up most of the space inside the tubing and also promote the flow of the eluent to the tubing wall where exchanges of sodium ions and hydrogen ions take place. The regenerant flows through the outer tube in the opposite direction. The void volume in the fibre suppressor is reduced to about 200 µL and consequently the band spreading is also reduced. Since this fibre suppressor provides continuous regeneration, it is not necessary to shut down the ion chromatograph. Despite the tremendous convenience, the fibre suppressor frequently traps air bubbles which when released will produce erroneously high signals. Furthermore, due to its lower exchange capacity, it is not compatible with gradient elution.

The latest type of suppressor, presently in use in the WQS for the separation of chloride, nitrate, and sulphate, is the anion micromembrane suppressor (AMMS). It was introduced by Dionex in 1985 and is based on the same regeneration mechanism as the fibre suppressor. The difference is the construction (Figure 3). In the AMMS, the eluent flows through a screen in a cell sandwiched between two ultrathin flat cation exchange membranes which are superimposed with compartments and screens on both sides. The regenerant flows through the two outer compartments countercurrently. The high-capacity ion-exchange screen serves the same functions as the polymer beads in the fibre suppressor by providing faster exchange of ions between the eluent and the regenerant and by reducing the void volume to about 45 µL. Therefore the AMMS improves mass transfer between the eluent and regenerant(1), is much less likely to trap air bubbles, has high capacity for the use of a wide range of eluents at much higher concentrations, and has the capability for gradient elution.

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A comparison of the three types of suppressor is given in Table I. Although skill is required for the preparation and repair of the fibre suppressor(4) and despite its limitations this suppressor's performance has been satisfactory in our IC Lab. In 1989 Dionex stopped producing the fibre suppressors and encouraged the Dionex ion chromatograph users to switch to the micromembrane suppressor. The purpose of the study is to determine whether the AMMS is suitable for our applications in the IC Lab.

## Experimental

### Apparatus

This study was conducted on the RMDS04 Workstation which is based on the Dionex QIC ion chromatograph. This workstation accepts sample matrices of surface water, domestic water, industrial waste, sewage effluent, landfill leachate and soil extract. The major components are listed below.

1. Eluent Delivery Pump: Single piston mini-pump. Operating flow rate at 0.77 to 7.7 mL/min, Laboratory Data Control Division, Milton Roy Co.
2. Pressure Gauge: Maximum pressure at 2000 psi. Dionex Corporation.
3. Injector: Air-operated pneumatic 6-port valve, Rheodyne Inc.
4. Interface: A built-by-WQS electronic unit which contains an infra-red relay switch and a solenoid which is made by Skinner Electrical Valves. It triggers the movement of the sampler and the injector.
5. Guard Column: One 5-cm HPIC-AG1 column, Dionex Corporation.
6. Separator Column: Two 5-cm HPIC-AG3 columns, Dionex Corporation.
7. Suppressor: Anion micromembrane suppressor, AMMS-1, maximum eluent flow at 3.0 mL/min, Dionex Corporation.
8. Detector: Multi-range conductivity detector, Dionex Corporation.

### Accessories

1. Sampler: Model SC15/TD15T, Gilson.
2. Peristaltic Pump: Piper Pump, Watson Marlow.

3. Integrator: Model 4270, Varian Associates, Inc.
4. Recorder: Dual pen chart recorder, Model 585, Linear Instrument Corp.
5. Air: Compressed cylinder of dry air, Matheson Gas Products, Canada.
6. Balances: Analytical balance, accurate to 0.0001 g and top-loading balance.

Reagents

The standards and reagents were prepared in deionized distilled water (DDW) of less than 1 µS/cm conductivity.

1. Sodium Chloride (NaCl): Anhydrous analytical grade.
2. Potassium Nitrate ($KNO_3$): Anhydrous analytical grade.
3. Sodium Sulfate ($Na_2SO_4$): Anhydrous analytical grade.
4. Sodium Bicarbonate ($NaHCO_3$): Anhydrous reagent grade.
5. Sodium Carbonate ($Na_2CO_3$): Anhydrous reagent grade.
6. Sulfuric Acid ($H_2SO_4$): Concentrated reagent grade.
7. Calibration Stock Solution,
   (400 mg/L as Cl, 400 mg/L as N and 2000 mg/L as $SO_4$):
   0.6594 g sodium chloride, 2.8876 g potassium nitrate and 2.9576 g sodium sulfate were accurately weighed and transferred into a 1 L volumetric flask. They were dissolved and diluted to the mark with DDW.
8. High Test Solution (60% of full scale),
   (12 mg/L as Cl, 12 mg/L as N and 60 mg/L as $SO_4$):
   30 mL of the Calibration Stock Solution was pipetted into a 1 L volumetric flask and diluted to the mark with DDW.
9. Low Test Solution (5% of full scale),
   (1 mg/L as Cl, 1 mg/L as N and 5 mg/L as $SO_4$):
   5 mL of the Calibration Stock Solution was pipetted into a 2 L volumetric flask and diluted to the mark with DDW.
10. Stock Eluent (0.3 M $NaHCO_3$ and 0.24 M $Na_2CO_3$): 25 g sodium bicarbonate and 25 g sodium carbonate were weighed on a top-loading balance and transferred to a 1 L volumetric flask. They were dissolved and diluted to the mark with DDW.

11. Working Eluent (0.003 M $NaHCO_3$ and 0.0024 M $Na_2CO_3$): 200 mL of the Stock Eluent was diluted to 20 L with DDW in a collapsible plastic container.
12. Regenerant (0.025 N $H_2SO_4$): 14 mL of concentrated sulfuric acid was diluted to 20 L with DDW in a collapsible container.
13. Sodium Hypochlorite (NaOCl): 5% w/w bleach, Javex.
14. Cleaning Solution (0.5% w/w NaOCl): Dilute 10 mL bleach to 100 mL with DDW

**Procedure**

In January 1990, a brand new unit of AMMS was installed for testing purposes on the RMDSO4 Workstation by connecting the eluent side of the device between the last separator column and the detector, and by joining the regenerant side to the peristaltic pump tubing with plastic couplers. This process was much simpler and easier as compared with the modification necessary for the fibre suppressor(4). The regenerant was pushed through the suppressor at 5.0 mL/min.

This Workstation accepts different types of "clean to dirty" samples containing chloride, nitrate, sulphate and other components at various concentration levels. Therefore, the AMMS was put through a vigorous testing using the most diverse sample types available.

When there were sufficient samples to start an analytical run, the ion chromatograph was set up by following the procedure given in the HAMES(5). The operating parameters are listed in Table II. After obtaining a stable baseline, DDW, High Test Solution and Low Test Solution were injected in the above order to monitor the performance of the chromatographic system. The chromatograms were evaluated regarding the presence/absence of expected peaks (water, chloride, nitrate and sulfate), their peak shapes and peak separations. If the separation and peak shapes were satisfactory, calibration would be carried out followed by the analyses of submitted samples as usual. At the end of the analytical run, the performance of the IC system was evaluated again using the High Test Solution and the number of samples analyzed were recorded. Replacement of column(s) and cleaning of the AMMS were promptly and accurately recorded.

If the separation of the nitrate and sulfate peaks was not satisfactory, the AG1 column was replaced and the system was evaluated. If the separation was again unsatisfactory, the first AG3 column was replaced followed with another evaluation. If again the separation was unsatisfactory, the second AG3 column was replaced followed by yet another evaluation. If all the above steps failed, the AMMS was evaluated by examining the peak shape of the sulfate peak of the Low Test Solution. Significant tailing indicated contamination of the AMMS and this happened about once a month. The device was removed and cleaned with 0.5% (w/w) sodium hypochlorite at 2 mL/min for 10 min, followed with a DDW rinse at the same flow rate for 30 min. When the cleaning process failed to improve the peak shape of sulfate even after two cleanings, the micromembrane unit was considered useless and would be replaced. The sequential steps are given in Table III. If the unit showed leaking at the side, it would also be discarded because it could neither be secured by tightening nor taken apart for servicing.

## Results and Discussion

### Fibre Suppressor

To establish the performance of the fibre suppressor, the High Test Solution was injected twice. The chromatograms, as shown in Figure 4, were evaluated and would be used for comparison against those obtained with the AMMS. The peaks of chloride, nitrate and sulfate are sharp, quite symmetrical (no significant tailing) and well separated from each other. It should be emphasized that the fibre suppressors, as modified by B. Wright, have been performing well in our IC Laboratory since 1984.

### Anion Micromembrane Suppressor (Serial Number 5126)

After replacing the fibre suppressor with an anion micromembrane suppressor (S/N 5126), another series of chromatograms of the High Test Solution and Low Test Solution was obtained. As shown in Figure 5, the chloride, nitrate and sulfate peaks produced in this set-up have comparable separation and peak symmetries to the system with the fibre suppressor. The slightly taller peaks and slightly less peak separation are due to the slightly shorter retention times. Since the AMMS unit was performing satisfactorily, it was left on the ion chromatograph and used for the analysis of routine samples under close observation for any changes in performance. In other words, the nitrate and sulfate peaks should be well separated, the sulfate peak should be taller than the nitrate peak and the sulfate peak in the Low Test Solution should be discernible and not show significant tailing.

Although the hydrophilic AG1 guard column and the hydrophobic AG3 separator columns protect the AMMS from corrosive attack of acids and alkalis and contamination of organic materials, after two weeks of usage (309 samples plus the calibration and QC solutions), the suppressor was inadvertently damaged by very acidic MISA sample solutions. Even though it was cleaned twice with sodium hypochlorite solution, the sulfate peak of the High Test Solution is shorter than the nitrate peak and worse yet, the sulfate peak of the Low Test Solution was not detected (Figure 6). Since its performance did not improve after two cleanings, this unit was replaced on January 19, 1990 by another new AMMS.

### Anion Micromembrane Suppressor (Serial Number 5095)

The second AMMS unit (S/N 5095) was installed on January 19/90 for evaluation. Its performance, as shown by the first series of chromatograms of the High Test and Low Test Solutions in Figure 7, was acceptable and comparable to that of the previous micromembrane suppressor in Figure 5. It was satisfactorily used for 24 months under normal operating conditions: i.e. the absence of physical abuse and corrosive samples. When this suppressor showed leaking at the side from the regenerant compartment, a sign of irreparable damage, the project was terminated on December 3/91. At that time it had been used for 20,000 samples plus calibration and quality control solutions. The cost was approximately 4.2 cents per sample.

## Conclusion

The testing unit (S/N 5095) of AMMS was used for "clean" samples of drinking water as well as for "dirty" samples of sewage, totalling over 20,000 analyses. Despite the limitations on its operating pressure of <60 psi and eluent flow rate of <3 mL/min, the AMMS is a rugged and suitable suppressor for our ion chromatographs. It can be quickly installed without modification and easily cleaned. Encouraged by the initial success of this study, we have installed additional AMMS on all the ion chromatographic workstations. Our conclusion is further confirmed by the assessments of all the other 8 units we have used since the start of this project.

## New Suppression Devices

### Electrodialytic Membrane Suppressor

A new type of suppressor has recently been developed in Japan(6). It is an electrodialytic membrane suppressor (EDMS) based on electrodialysis with cation exchange membrane at constant

applied potential and is used for anion chromatography with conductometric detection.

The EDMS consists of an anode, a cathode, a cation exchange membrane in the $H^+$ form, and a sulfuric acid regenerant flow passage. Like the three types of suppressors described in this report, when carbonate/hydrogen carbonate eluent and sample anions were introduced into the EDMS, the eluent and sample anions were converted to carbonic acid and the corresponding acids respectively. When the eluent of 1.6 mM $Na_2CO_3$/2.0 mM $NaCO_3$ was used for anion chromatography, the EDMS reduces the eluent conductivity from about 570 to 13 µS/cm with enhancement of conductivity for the anions at applied potential of approximately 5V. The EDMS has been successfully applied to the determination of anions in rain and soil waters by ion chromatography .

In the Ion Chromatography Laboratory of the WQS, the conductivity of the eluent of 2.4 mM $Na_2CO_3$/3.0 mM $NaCO_3$ was reduced from about 600-1000 µS/cm to about 10-20 µS/cm using the AMMS(2). Therefore the two devices, AMMS and EDMS show comparable performance in suppression. If the need arises, the suitability of the EDMS for our applications could be investigated.

## Self-Regenerating Suppressor

A more recent development, the "Self-Regenerating Suppressor" (SRS) was introduced by Dionex Corp. in 1992(7). It is similar to the MicroMembrane Suppressor except regenerant ions are produced in situ by electrolysis of water. This is achieved by incorporating electrodes inside the regenerant chambers. Hydronium and hydroxide ions required for the respective suppression reactions are generated by the electrolysis of water at the electrode surface, and external acid or base supply are unnecessary. According to Dionex Corp, the application of high-performance suppressed ion chromatography with SRS has become much easier as it requires no operator involvement and is maintenance-free.

However, this device is not compatible with organic matters in the eluent. Therefore doping the eluent with organics or analyzing samples containing high levels of organic matters should be avoided. At this time, the Ion Chromatography Lab finds the AMMS completely acceptable and does not want to invest in a new accessory. We shall continue to prepare the regenerant of dilute sulfuric acid solution and watch for new developments in suppressor technology for ion chromatography.

## References

1. H. Small: "Ion Chromatography." Plenum Press, New York and London (1989).

2. F. Lo: Report on the Study of the Ion Chromatographic Systems in the Water Quality Section. Internal Report, WQS, LSB, Ministry of the Environment (1990).

3. J. Crowther and J. McBride: Analysis of Precipitation Samples by Ion Chromatography, Part I - Determination of Anions. Internal Report, WQS, LSB, Ministry of the Environment (1978).

4. J. Crowther and B. Wright: Fibre Suppressors for Ion Chromatographic Systems - Modification and Operation. Internal Report, WQS, LSB, Ministry of the Environment (1984).

5. The Determination of Sulphate in Surface Water, Domestic Water, Sewage, Industrial Waste, Leachate and Health Samples by Automated Ion Chromatography. Method Number 3172A, Laboratory Services Branch, Ministry of the Environment (1992).

6. K. Ohta, H. Matsui and K. Tanaka: Anion Chromatography with Conductometric Detection Using Electrodialytic Membrane Suppressor. Bunseki Kagaku, 39, 457-461 (1990).

7. A. Henshall, S. Rabin, J. Statler and J. Stillian: A Recent Development in Ion Chromatography Detection: The Self-Regenerating Suppressor. American Laboratory, November 20R-20Z (1992).

## Table I

Comparison of Dionex Chemical Suppressors

| Feature | Column | Fibre | Micromembrane |
|---|---|---|---|
| Year introduced | 1975 | 1983 | 1985 |
| Medium | ion exchange resin | ion exchange | semi-permeable membrane |
| Max. Pressure | highest | 200 psi | 50 psi |
| Continuous regeneration | no | yes | yes |
| Sensitivity | excellent | excellent | excellent |
| Capacity | high | low | high (10-15 X fibre) |
| Void volume | 2000 µL | 200 µL | 45 µL |
| Gradient capability | no | no | yes |

## Table II

Operating Parameters of the Ion Chromatograph

| | |
|---|---|
| Instrument: | Dionex, Model QIC. |
| Sample: | 12 mg Cl/L, 12 mg N/L, and 60 mg $SO_4$/L. |
| Sample volume: | 0.05 mL. |
| Columns: | One HPIC-AG1.<br>Two HPIC-AG3. |
| Eluent: | 0.003 M $NaHCO_3$ and 0.0024 M $Na_2CO_3$ at 2.5 mL/min. |
| Suppressor: | Anion micromembrane suppressor (AMMS-1), Dionex. |
| Regenerant: | 0.025 N $H_2SO_4$ at 5.0 mL/min. |
| Detector: | Conductivity at 30 µS/cm full scale. |
| Integrator: | Varian, Model 4270. |
| Mode: | Peak height. |
| Recorder: | 0.5 V full scale |
| Chart speed: | 20 cm/hr. |

## Table III

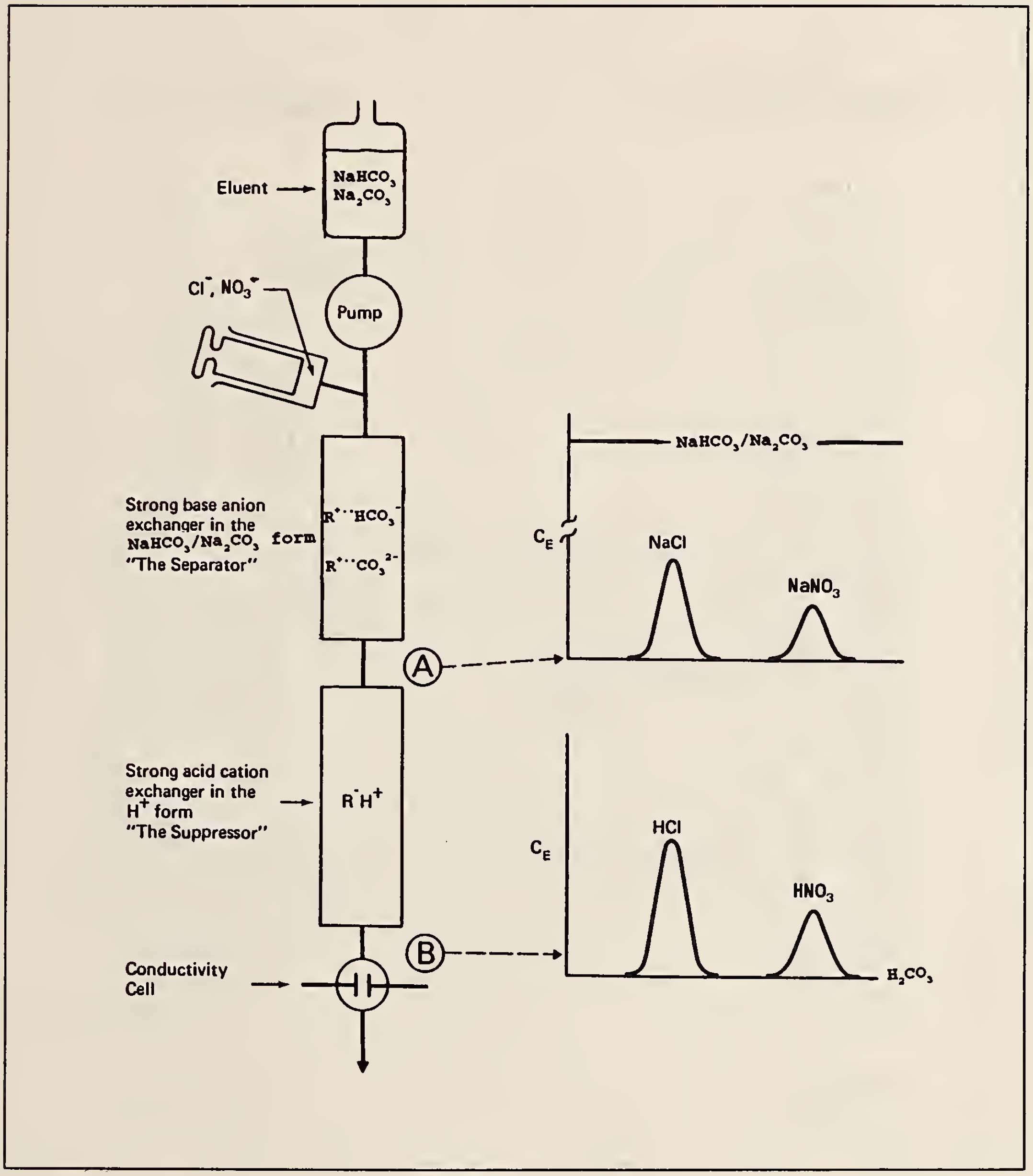
## Monitoring Performance of IC System

| Step | AG1 column | First AG3 column | Second AG3 column | AMMS |
|---|---|---|---|---|
| 1 | old | old | old | old |
| 2 | new | old | old | old |
| 3 | new | new | old | old |
| 4 | new | new | new | old |
| 5 | new | new | new | clean or replace |

Examine the chromatograms of the High and Low Test Solutions. If the performance is not satisfactory, proceed one step at a time until satisfactory results are obtained.

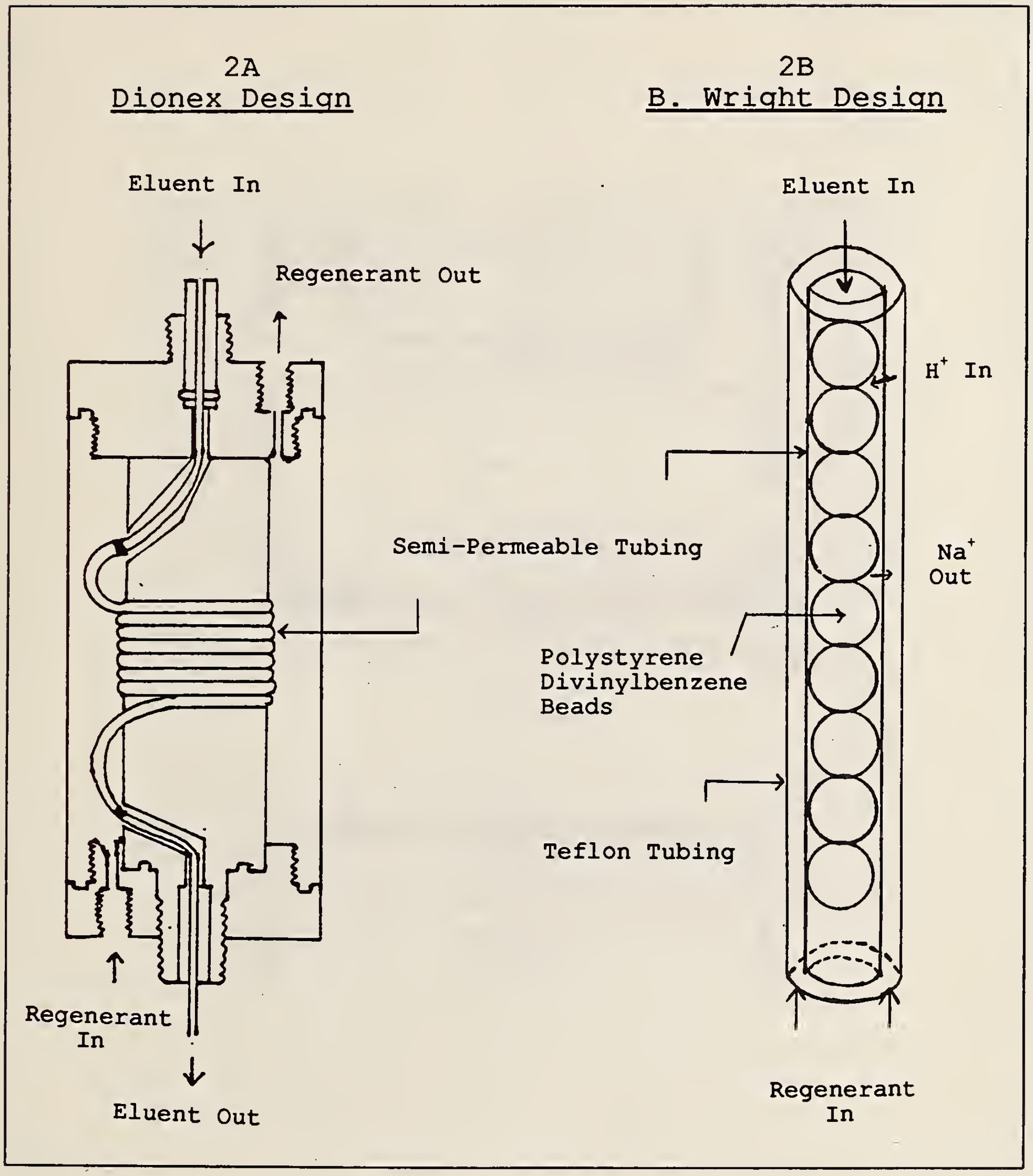
**Figure 1**

Suppressor Column for Anion Separation



## Figure 2

Fibre Suppressor



## Figure 3

Micromembrane Suppressor

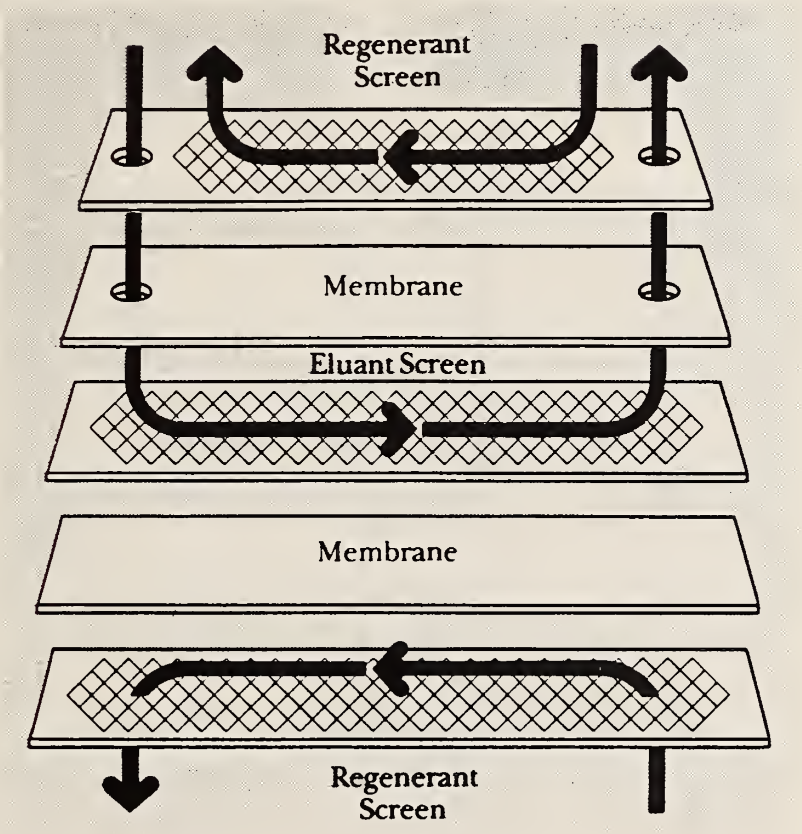


**Figure 4**

Chromatograms Using Fibre Suppressor

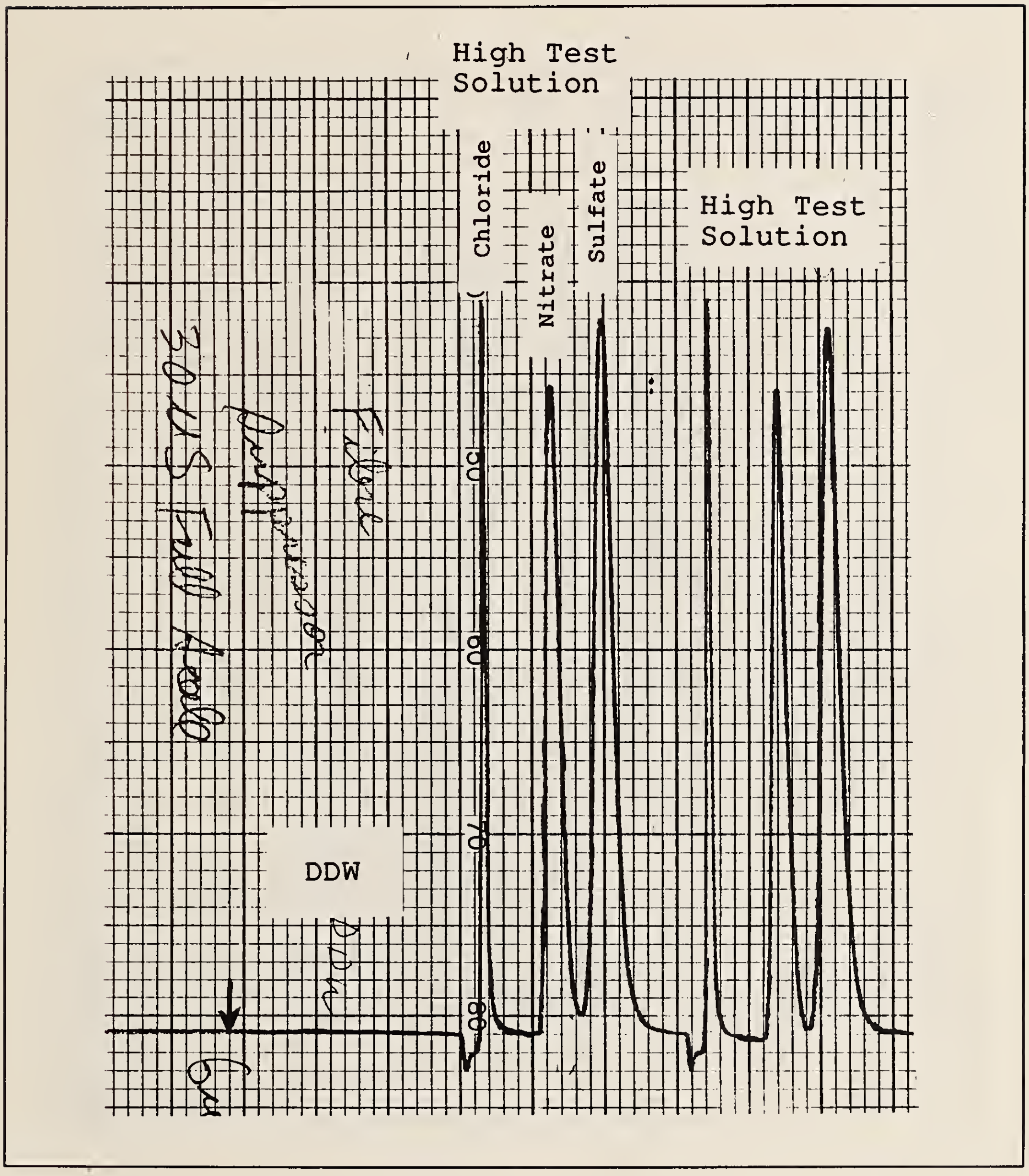


Figure 5

Chromatograms Using Micromembrane Suppressor (S/N 5126)

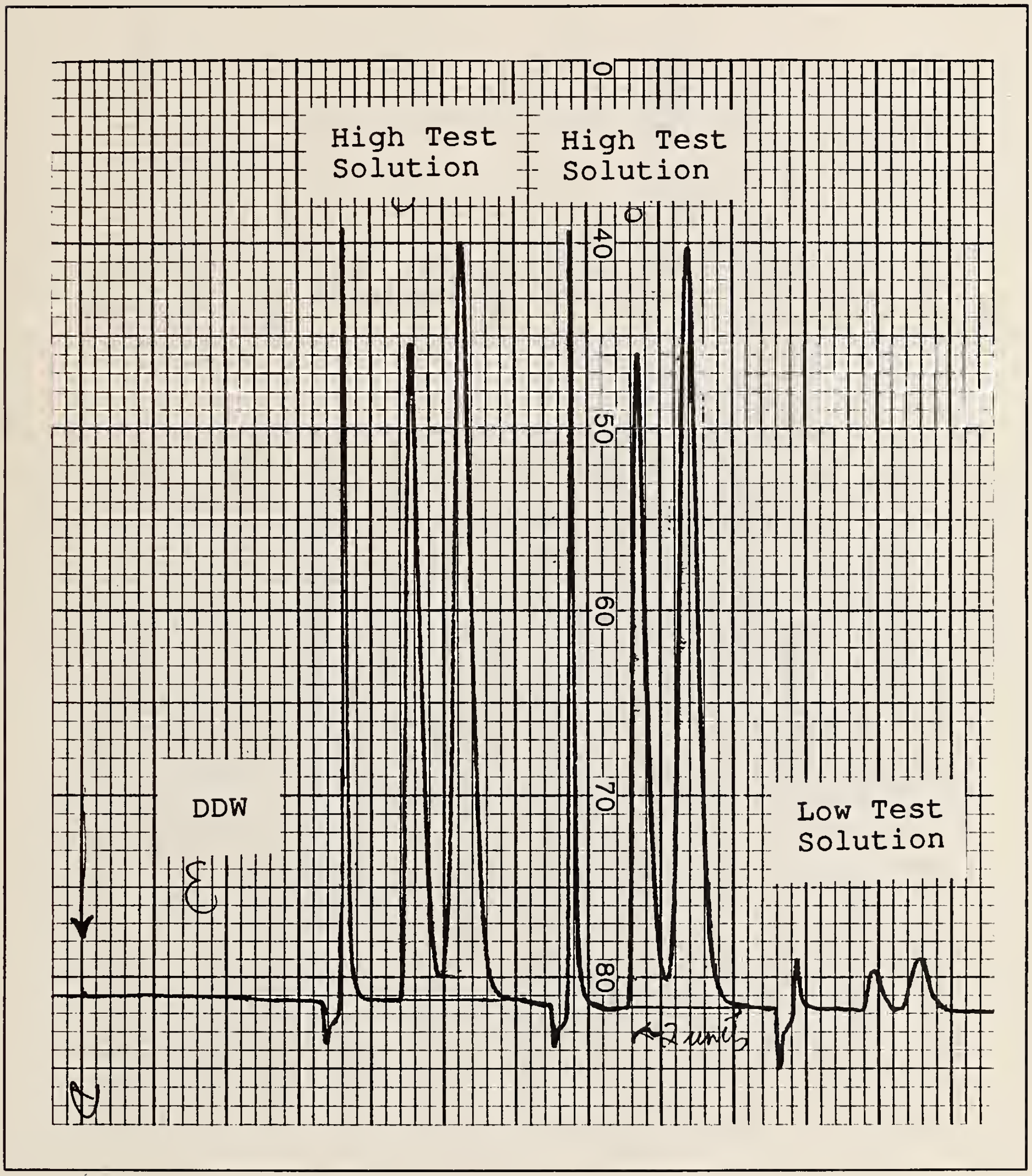


**Figure 6**

Chromatograms Using Damaged Micromembrane Suppressor (S/N 5126)

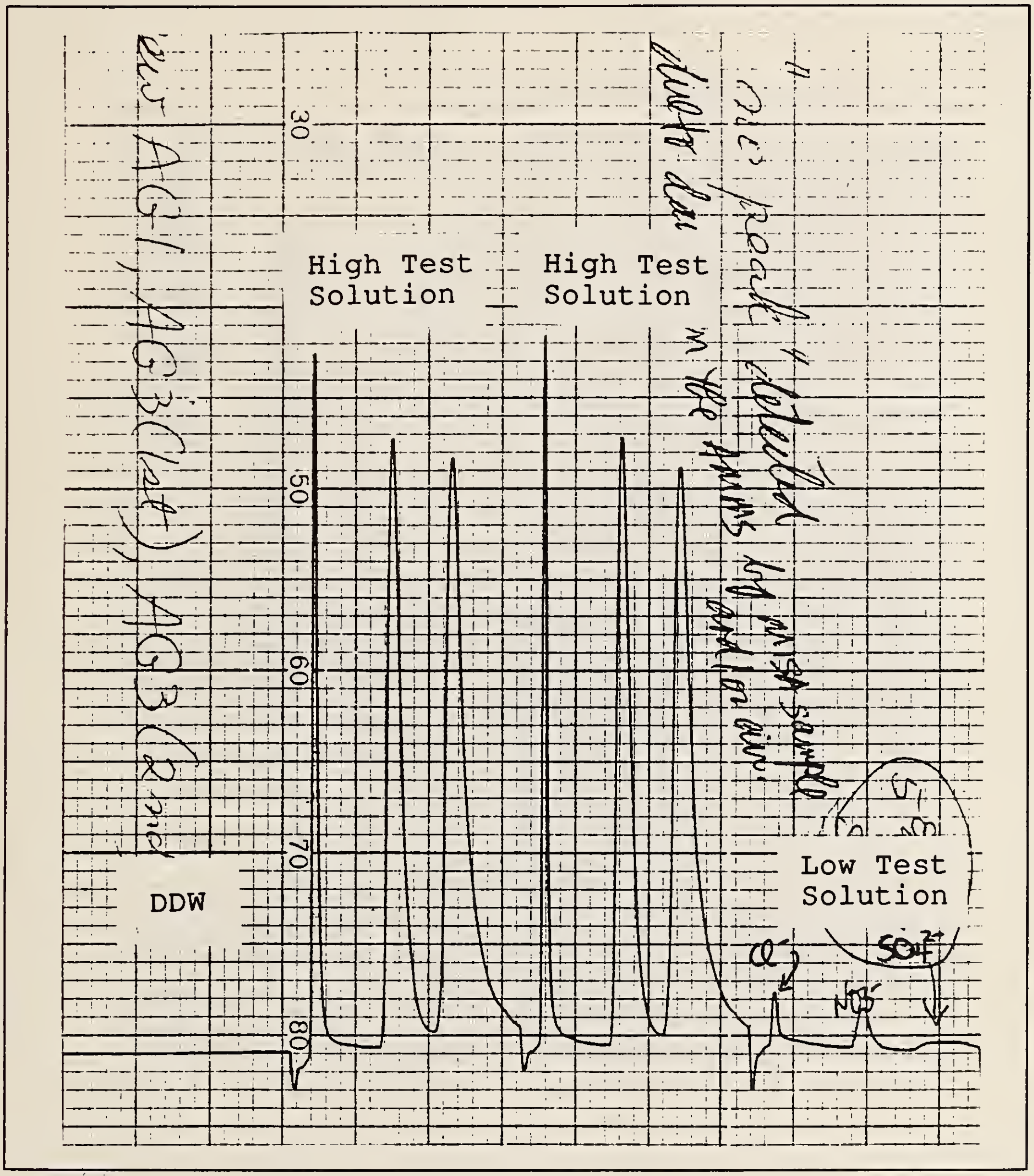
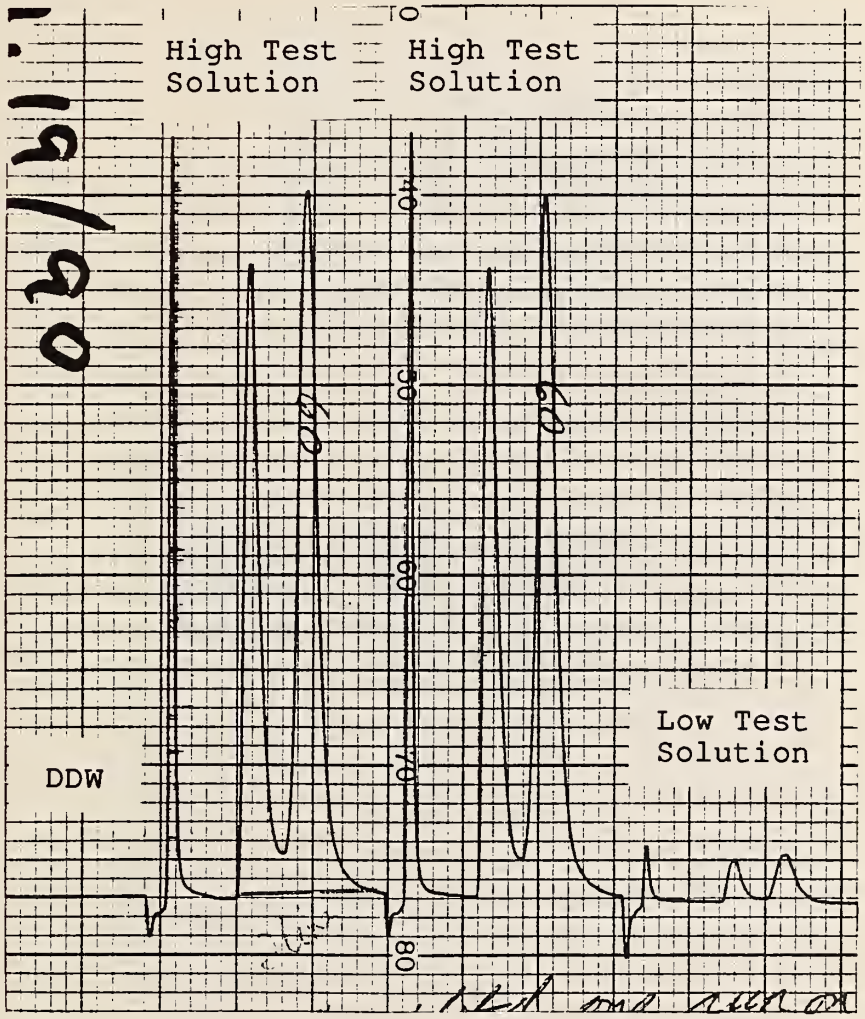


**Figure 7**

Chromatograms Using Micromembrane Suppressor (S/N 5095)



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Evaluation of Dionex anion micromembrane suppressor in the ion chromatography laboratory
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